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Can Gold be an Effective Catalyst for the Deacon Reaction?

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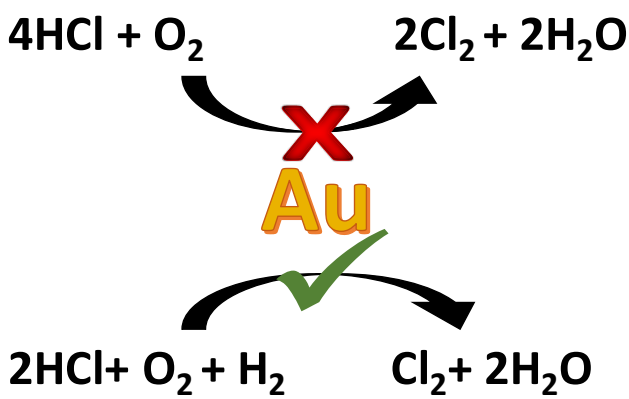
Abstract
The Deacon reaction is an important industrial process for the oxidation of hydrogen chloride, thereby enabling chlorine to be recycled. As gold is an efficient catalyst for reactions involving hydrogen chloride and oxygen, we have studied the use of gold as a potential catalyst for the Deacon reaction. Unfortunately, gold displays only limited activity; however, this is markedly increased if hydrogen is cofed as a reactant.

Graphic Abstract



Keywords Deacon process · Hydrogen chloride · Chlorine · Gold catalyst

1 Introduction

Chlorine is an important commodity chemical that is used in many applications. During use hydrogen chloride is often made as a by-product. Although hydrogen chloride has applications in the chemical industry, such as the hydrochlorination of acetylene, in many cases it is important that the chlorine is recovered. The Deacon reaction [1] is the industrial process whereby hydrogen chloride is oxidized to chlorine and water thereby permitting chlorine recovery for reuse. Due to equilibrium conditions, low operation temperatures are favorable in terms of possible conversion per pass.

$$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$$

Ekkehard Schwab now retired from BASF SE.

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The Deacon reaction, named after its inventor Henry Deacon, was commercialised in 1874. The first catalysts used were copper chlorides which were not stable above 400 °C and would start to evaporate when the operating temperature was 430–475 °C. Since then there has been a substantial effort to increase the conversion efficiency of the reaction. The Shell-Chlor process [2] introduced in the 1960s used $CuCl_2$–KCl/SiO_2 catalysts with a single fluidized-bed reactor, but the project was discontinued due to severe corrosion problems. Totsis et al. [3, 4] used copper-based catalysts in a dual fluidized-bed reactor which they developed to achieve a high HCl conversion to Cl_2 with limited corrosion. Nieken and Watzenberger [5] employed a two-step fixed-bed reactor configuration to overcome corrosion problems. Sumitomo Chemicals subsequently developed a RuO_2–TiO_2 catalyst in a fixed-bed reactor [1]. The RuO_2/TiO_2 catalyst was found to exhibit both high activity at low temperature and stability. The rutile phase of TiO_2 is the most effective form since it leads to improved growth of the epitaxial layers and this enable the catalyst to be very stable and active [6]. BASF researchers subsequently developed a K promoted RuO_2/Al_2O_3 catalyst [7]. Further improvements for the RuO_2 catalysts were reported by Mondelli et al. [8] using a RuO_2/SnO_2–Al_2O_3 catalyst in 2011 and by Teschner et al. using a RuO_2–SnO_2 catalyst [9]. Amrute et al. [10] reported CeO_2 based catalysts but these were less active when compared with RuO_2. They also studied Cr_2O_3 which has higher activity and stability than Cu based catalyst but leads to formation of chromyl chloride [11]. Based on these studies they subsequently investigated a delafossite $CuCrO_2$ catalyst, which they found to be stable [12] but significantly less active than RuO_2.

The proposed mechanism of the Deacon reaction can be divided into two steps; firstly, HCl adsorption by a metal oxide to form a metal (oxy)chloride. Secondly, oxidation of this species by O_2 to regenerate the metal oxide and free Cl_2. The mechanism proposed by Lopez et al. is based on experimental and DFT calculations using RuO_2/TiO_2 as a catalyst [6] involving the main steps of hydrogen abstraction from HCl, recombination and desorption of atomic chlorine, hydroxyl recombination, water desorption, and oxygen adsorption. As Au-based catalysts have a high hydrogenation rate for an oxygen molecule, we considered that these steps could be achieved in parallel over Au. RuO_2 is also among the model compounds for various oxidation processes such as CO, H_2, CH_4 [6] as are Au-based catalysts presently.

In a recent review, Over and Schomäcker [13] proposed that the dissociation energy of molecular oxygen could be used as a promising descriptor for activity with catalysts for which the oxygen dissociation energy was in the range 0 to − 100 kJ/mol gave the highest activity. This observation further prompted us to consider whether supported Au catalysts could be used for the Deacon reaction as the oxygen dissociation energy is − 48 to − 57 kJ/mol [14]. We were further prompted to investigate the use of Au for this reaction since Au/C catalysts have been found to be very active for acetylene hydrochlorination [15] and CO oxidation [16] and hence can use both HCl and O_2 as substrates. In this study we report an investigation into the possible activity for Au in the Deacon reaction.

2 Experimental Methods

2.1 Materials

$RuCl_3 \cdot 3H_2O$ (Aldrich, 99.98%), $HAuCl_4 \cdot 3H_2O$ (Aldrich ≥ 99.9%), TiO_2-rutile (nano-powder, Aldrich, 99.5%), $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich, 99.999%), ethanol (as abs. ethanol, Fisher Scientific), Na_2CO_3 (Fisher Scientific, anhydrous) and NaOH (VWR, pelleted ≥ 97%) were used as received. Deionised water provided in house. Gases used as received were 5% HCl/bal. Ar (BOC) and argon (Air Products). Moisture was removed from compressed air (in house) by passing through a filter containing molecular sieves prior to entering the reactor and similarly the 2% H_2/bal. air (BOC) was dried by means of molecular sieves and an Agilent Technologies Gas Chromatograph moisture filter.

2.2 Catalyst Preparation

7 wt% RuO_2/TiO_2 was prepared by deposition–precipitation of $Ru(OH)_2$. The TiO_2 rutile support (5 g) was dispersed in distilled water (250 ml) under continuous stirring. Then, an appropriate amount of $RuCl_3 \cdot 3H_2O$ dissolved in 50 ml of distilled water was added to the slurry. Precipitation of $Ru(OH)_2$ was attained by adding an aqueous NaOH solution (10 wt%) drop-wise to the slurry until pH 12 was attained. The suspension was kept at room temperature for 1 h and then heated to 65 °C for 1 h with stirring. The suspension was cooled, filtered and washed with distilled water until the pH of the washing water was neutral, the material was dried at 120 °C, and calcined in static air at 500 °C (10 °C/min) for 5 h.

5 wt% Au/TiO_2 was prepared using the deposition–precipitation method [17]. To prepare the catalyst (ca. 1 g) $HAuCl_4 \cdot 3H_2O$ (4.08 ml, 12.25 mg/ml) and TiO_2 (0.95 g, rutile) were added to distilled water (100 ml) with vigorous stirring. This mixture was heated to 60 °C and the pH was adjusted to pH 7 by the slow addition of aqueous NaOH (0.1 M). The solution was left stirring for 1 h at the final pH before cooling in ice for 20 min. The catalyst was then recovered by filtration, washed with distilled water until the pH of the washing water was neutral and dried in air (110 °C, 16 h).

5 wt% Au/CeO_2 was prepared using the deposition precipitation method in an analogous way. Ceria was synthesised from $Ce(NO_3)_3 \cdot 6H_2O$ (2.5 g) which was dissolved in ethanol and stirred for 1 h, then left to evaporate. The recovered solid was then calcined for 6 h at 550 °C (1 °C/min). Deionised water (400 ml) was heated to 60 °C and an appropriate amount of $HAuCl_4 \cdot 3H_2O$ was then added and stirred for 15 min. The ceria (2 g) was then added and 0.5 M Na_2CO_3 was added until pH 8 was reached and the slurry was then left for 1 h before filtering. The solid was washed with 1 l of hot deionised water and then dried at 110 °C for 5 h. The dried material was calcined at 500 for 5 h (10 °C/min). The resulting catalysts comprised metallic Au with 2–5 nm nano-particles as described previously [17].

All catalysts were pelleted and sieved to between 400 and 600 µm prior to loading in the reactor.

2.3 Catalyst Characterisation

Powder X-ray diffraction (XRD) analysis of the catalysts was carried out on a PANalytical X'pert Pro powder diffractometer (Malvern Panalytical, Malvern, UK) using a Cu source operated at 40 keV and 40 mA with a Ge (111) monochromator to select Kα1 X-rays. Patterns were analysed from measurements taken over the 2θ angular range 10°–80° (step size of 0.016°).

Scanning electron microscopy (SEM) was performed on a Tescan Maia3 (Tescan Orsay Holding, a.s., Czech Republic) field emission gun fitted (FEG-SEM) with an Oxford Instruments XMAXN 80. Images were acquired using the secondary electron (SE) and backscattered electron detectors (BSE). Samples were dispersed as a powder onto adhesive carbon Leit discs mounted onto aluminium stubs. Particle size distributions were recorded manually with a minimum of one hundred particles being examined.

2.4 Deacon Reaction

A reactor for the Deacon reaction was constructed wholly of Hastelloy C-276® (Supplementary Fig. S1). The gases (5% HCl/bal. Ar and dry air or dry 2% H_2/bal. air) were individually fed via calibrated mass flow controllers and mixed prior to flowing to the heated reactor (tube O.D. 0.375″, I.D. 0.236″). All lines prior to and after the reactor oven were heated to 100 °C to prevent condensation. The reactor tube was filled with alumina spheres (diameter 0.6 mm) before and after the catalyst bed (Fig. S1c). Typically, catalyst (250 mg) was placed between quartz wool at the centre point of the reactor tube, which itself was placed in a PID controlled reactor oven (± 1 °C). The reactor effluent passed through an aqueous trap to dissolve the unreacted HCl and enable the HCl conversion to be calculated using an acid base titration. At ambient pressure, 4.39% HCl and 2.59% O_2 were passed through the reactor bypass (total flow 25 ml/min). The reactor containing catalyst (0.25 g) was then heated to 500 °C. When this reaction temperature was reached the bypass was switched so that the gases flowed over the reactor. Samples for titration were taken every 20 min and the reaction was continued for 4 h. Reactions in the absence of catalyst showed no conversion and a standard 7 wt% Ru/TiO_2 catalyst under these reaction conditions gave a steady state HCl conversion of 40% which under these reaction conditions is well below the equilibrium level of ca. 83% [18]. For reactions where H_2 was included 0.25% H_2 was added to the reaction gases. Argon was used to purge the reactor.

Reactant gases were passed into a liquid trap containing pre-weighed H_2O. These were exchanged periodically, and the loaded solutions titrated with a solution containing 0.1 M NaOH and with a phenolphthalein indicator to determine the HCl concentration. From this the conversion of HCl was calculated.

3 Results and Discussion

An initial reaction was carried out using the rutile–TiO_2 support and this showed very limited activity of ca. 1% conversion (Fig. 1). The data are shown for reactions after 60 min on-line at 500 °C as in the initial period HCl was adsorbed onto the catalyst/support; consequently, the data are shown when a steady-state activity was observed. The 5 wt% Au/TiO_2 catalyst showed a modest improvement in activity of

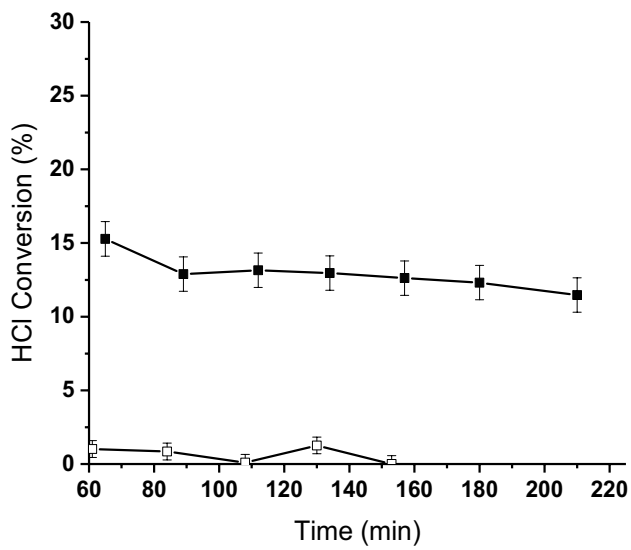

Fig. 1 Comparison of the HCl conversion over TiO_2 (open square) and 5% Au/TiO_2 (filled square) catalyst. Reaction conditions: Total flow = 25 ml/min; [HCl] = 4.39%; [O_2] = 2.59%; T = 500 °C; cat. = 250 mg

ca. 12% HCl conversion (Fig. 1). It should be noted that the equilibrium HCl conversion under these dilute reaction conditions at 500 °C is 72.7% (Supplementary Fig. S2). The catalyst was characterised by XRD and SEM prior to reaction in both the as-made and as-pelleted state (Supplementary Fig. S3). The diffraction patterns for both the fresh and pelleted catalysts were consistent with the rutile–TiO_2 diffraction pattern (JCPDS: 88-1175) with strong reflections at $2\theta = 27.6°$, 36.3° and 54.5°. No Au reflections (typically $2\theta = 38°$, 44° and 65°) are visible in the diffraction patterns and we consider that the adsorbed nano-particles are ≤ 5 nm in diameter. Electron microscopy (Supplementary Fig. S3) of the fresh and pelleted catalysts were obtained with the backscatter and in-line detectors and Au nano-particles are visible, however, in general these are < 7 nm in diameter. From the images the dispersion of Au does not appear efficient, with some aggregates of Au nano-particles present. However, this is close to the limit of the detector and previous work using a comparative preparation has shown particles ranging from 2 to 5 nm which has been shown to be optimal for many redox reactions [17].

It is clear that Au/TiO_2 is not an effective Deacon catalyst, as the activity for a reference 7 wt% RuO_2/TiO_2 catalyst gave ca. 40% HCl conversion at 500 °C for 3 h time-on-line under these conditions (Supplementary Fig. S4). We also investigated the 5 wt% Au/CeO_2 catalyst and CeO_2 at 500 °C under these conditions (Fig. 2) and in this case Au gave no increase in activity over that observed for the CeO_2 support. Over both materials the HCl conversion can be observed to decrease from ca. 25 to 15% from 120 min time-on-line. At this stage, we therefore concluded that Au is not an effective catalyst for the Deacon reaction, which suggests that using oxygen dissociation energy is not an appropriate indicator of activity for this reaction. It is possible that Au cannot simultaneously activate HCl and O_2. In the acetylene hydrochlorination reaction it is proposed that [15] the Au^+ initially activates HCl and the Au^+/HCl complex interacts with the acetylene and perhaps this pathway is not effective with O_2.

It is known that dioxygen cannot by itself initiate a radical reaction but can in effect propagate such reactions once an initial activation has been achieved. One such initiator can be molecular hydrogen, which will then lead to the formation of a reactive hydroperoxy species. Indeed, previous studies using gold catalysts for propene oxidation [19] have shown that selective oxidation to propene oxide requires the addition of H_2 as a co-reactant. With this in mind, we carried out the Deacon reaction under the same reaction conditions at 500 °C but with the addition of H_2 (0.25%). The results shown in Fig. 3 show that the catalyst activity can be improved for both TiO_2 and the 5 wt% Au/TiO_2 catalyst, with the effect being more marked when Au is present (Figs. 1 and 3). However, the steady state activity was still considerably lower that observed for the 7 wt% RuO_2/TiO_2 catalyst in the absence of H_2 (Supplementary Fig. S3). The observation that H_2 can enhance the Deacon reaction with TiO_2 alone is a very interesting observation. For the Au/TiO_2 catalysed propene epoxidation with H_2 and O_2 it is often discussed that activation occurs at the contact rim between the Au nano-particles and the support [20]. However, in this case activation of the H_2 is occurring without the need for the gold interfacial sites and this is an effect that warrants further investigation.

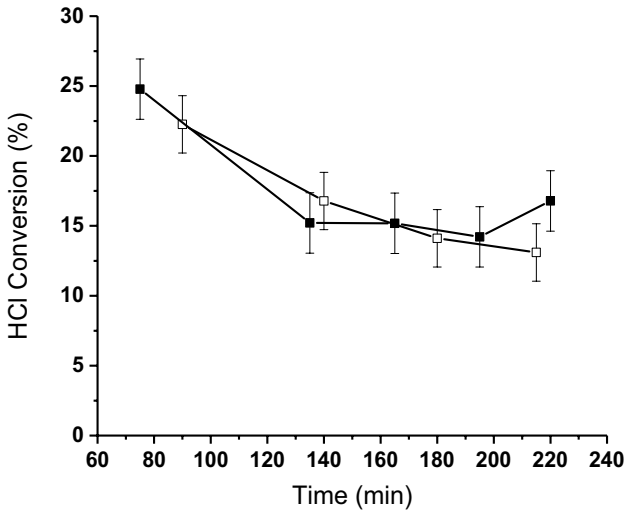

Fig. 2 Comparison of the HCl conversion over CeO_2 (open square) and 5% Au/CeO_2 (filled square) catalyst. Reaction conditions: Total flow = 25 ml/min; [HCl] = 4.39%; [O_2] = 2.59%; T = 500 °C; cat. = 250 mg

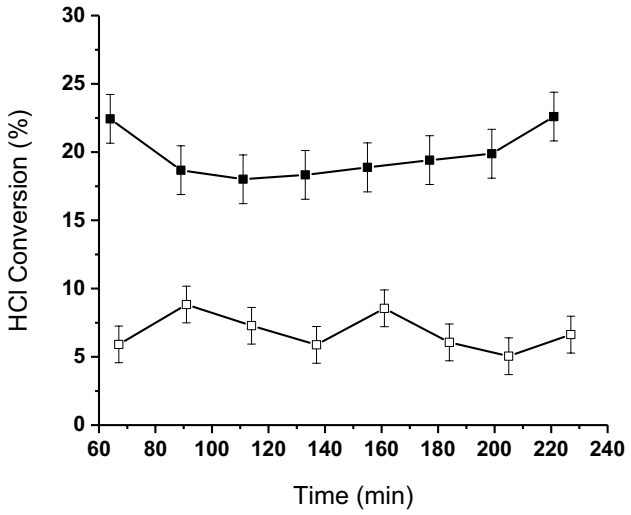

Fig. 3 Comparison of the HCl conversion over TiO_2 (open square) and 5% Au/TiO_2 (filled square) catalyst with H_2. Reaction conditions: Total flow = 25 ml/min; [HCl] = 4%; [O_2] = 2%; [H_2] = 0.25%; T = 400 °C; cat. = 250 mg

4 Conclusions

While gold can be an effective catalyst for a range of oxidation reactions and is acknowledged to be the best catalyst for acetylene hydrochlorination [15] our brief study shows that gold does not show promise for the Deacon reaction; gold is not able to simultaneously activate O_2 and HCl which is a requirement for the Deacon reaction. When H_2 is introduced as a co-reactant the situation changes and gold does display some Deacon activity.

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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